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Assessment of Diesel Particulate Control Direct and Catalytic Oxidation

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Assessment of Diesel Particulate Control: Direct and Catalytic Oxidation

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SECTION 1

INTRODUCTION

Diesel engines are becoming available in increasing numbers in passenger car service because of their good fuel economy in comparison to conventional gasoline engines. About 160,000 diesel-powered light-duty vehicles were sold in the 1978 model year in the United States. This figure is expected to double in 1979, and sales of light-duty diesels are expected to continue to increase substantially over the next 10 years. In 1990 15 to 20 percent of all light-duty vehicles sold are predicted to be diesel powered.

Though the diesel exhaust is relatively clean with respect to unburned hydrocarbons and carbon monoxide, it contains particulate emissions that are 30 to 50 times greater than those produced by the catalyst-equipped gasoline engine. These diesel particulate emissions will contribute to already high levels of total suspended particulate (TSP) in urban areas. Furthermore, certain components of the particulates have been identified as carcinogenic, thereby creating a potentially greater health hazard.

The U. S. Environmental Protection Agency (EPA) has issued an NPRM (Notice of Proposed Rule Making) which will impose limits on the amount of particulate that may be emitted by each light-duty diesel vehicle. The proposed standards, based on the presently used FTP with a particulate measurement procedure added, are 0.6 grams per mile (0.37 g/km) for 1981 model year vehicles and 0.2 grams per mile (0.12 g/km) for 1983 model year vehicles. These standards are based on the need to reduce (or prevent an increase in) the TSP levels in urban areas as diesels become more numerous. It is quite possible that even more stringent particulate emission standards will have to be set in the future to control the toxicity problem.

There are several approaches to the control of diesel emissions that are being pursued by the automotive industry, EPA, and others. These include operating mode modifications, engine design and component modifications, fuel modifications, and exhaust devices.

In this report we discuss the technology of and potential devices for: thermal and catalytic oxidation of particulate while suspended in the exhaust stream, thermal oxidation of filter-trapped particulate, catalytic oxidation of particulate, oxidation of particulate, oxidation of particulate

trapped by other techniques, and catalytic oxidation of the organic vapors before deposition on the particulate.

The following discussions will center primarily on the application of "add-on" devices in the engine's exhaust systems. However, the successful application of a thermal or catalytic oxidation system for particulate or organic vapor control may also depend on operating mode, engine design, or fuel modifications for maximum effectiveness. These aspects will also be covered in the discussions where appropriate.

SECTION 2

DIESEL PARTICULATE

The particulate matter emitted by the engine consists of solid, liquid, and adsorbed vapor. The particles can be considered either as single entities or as aggregates of subunits. Because of this complexity, exact specification is difficult; one must measure properties that seem to be meaningful in the design of control strategies. Moreover, each engine, fuel, and set of operating conditions causes the properties of the particulate to vary. In the following section we have tried to give representative values for some of the properties that are important in the design of control strategies.

PROPERTIES OF DIESEL PARTICULATE

Physical Form: Small, solid, irregularly shaped particles, agglomerates of roughly spherical subunits. High molecular weight HC adsorbed on surface. Also may have liquid coating.

Size: Number median diameter 0.3 μm; subunits about 10 nm

Size Distribution: See Figure 1[1] for sample size distribution.

Composition: Mostly carbonaceous material 10-50 percent extractable with organic solvent.

Bulk Density: $\rho_{bulk} \simeq 0.075 \frac{g}{cm^3}$

Ash: One value of 16 percent

Extractable Hydrocarbons: See Table 1[2]

Chemical Composition: See Table 2[2]

PARTICULATE EMISSIONS RATE CHARACTERISTICS OF DIESEL PASSENGER CARS

Measurements of light-duty diesel particulate emissions under various conditions of operation have been reported in the literature. These measurements provide some insight into the factors that influence the emission rate.

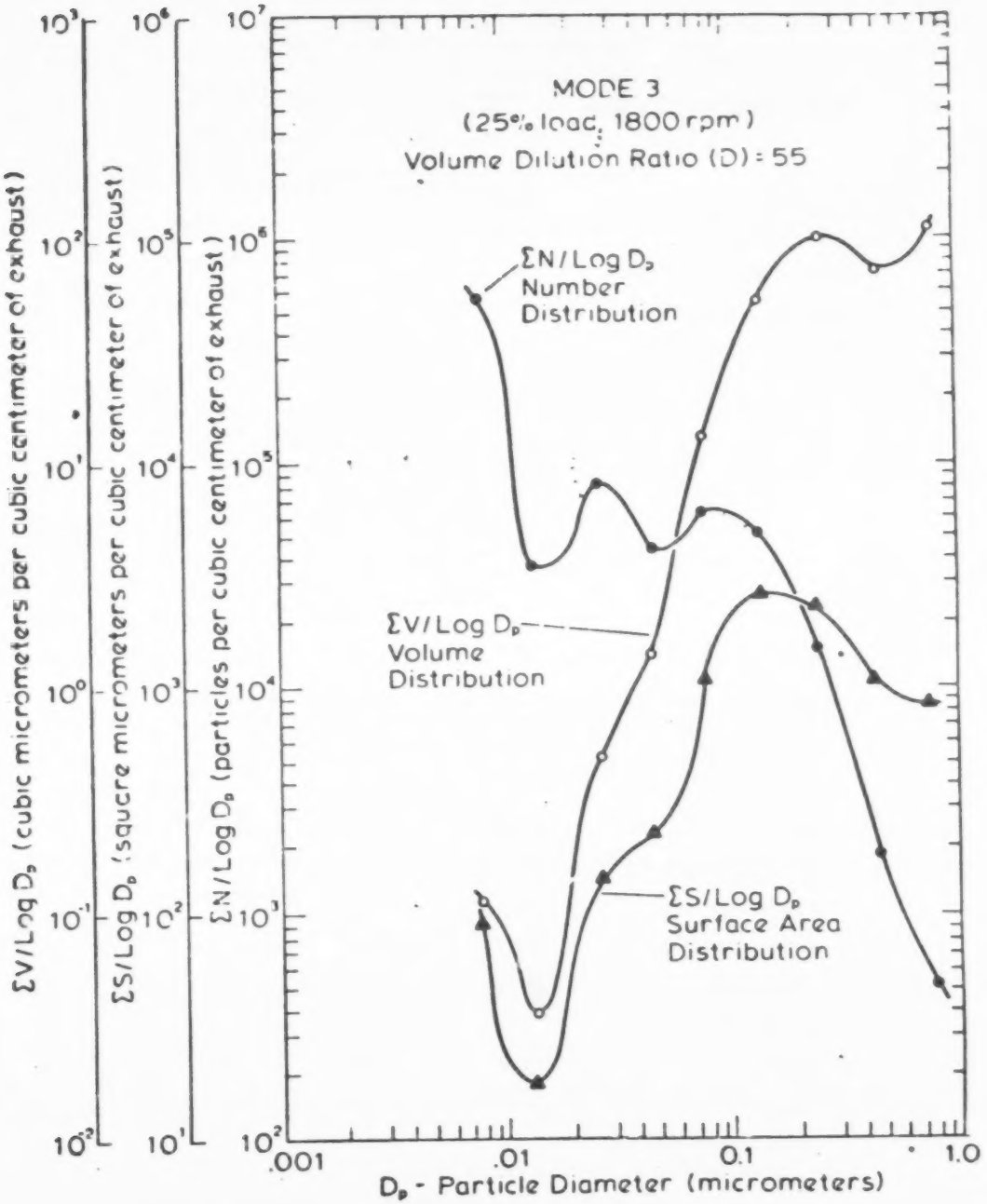

FIGURE 1. NUMBER, SURFACE AREA AND VOLUME DISTRIBUTIONS FOR MODE 3 OF THE EPA 13 MODE CYCLE

TABLE 1. SOLUBLE ORGANIC FRACTION AND SULFATE EMISSIONS FROM HEAVY-DUTY DIESEL (a)

	Soluble Organic Fraction	Sulfate Emissions
	% of Total Particulate	
Light Diesel Fuel	17	9
Average Diesel Fuel	16	9
Heavy Diesel Fuel	32	12

(a) Caterpillar naturally-aspirated, direct-injection V-8 engine, EPA mode 5, 8:1 dilution ratio.

TABLE 2. FRACTIONAL BREAKDOWN OF SOLUBLE ORGANIC EMISSIONS FROM HEAVY-DUTY DIESEL (a)

	Fuel Type		
	Light	Average	Heavy
Paraffin	43	43	56
Oxygenated	14	11	8
Aromatic	3	6	8
Transitional	6	3	3
Acid	10	15	10
Base	2	1	1
Ether and Hexane Insoluble	22	21	15

(a) Caterpillar naturally-aspirated, direct-injection V-8 engine, EPA mode 5, 8:1 dilution ratio.

Particulate emissions from passenger-car diesels range from 0.2 to 0.7 gm/km on the 1975 FTP cycle, and from 0.1 to 4.0 gm/km on steady speed/load operation. Expressed in terms of concentration in the exhaust gases, the particulates range from about 20 to 130 mg/m^3.

In general, the particulate emission rate is a function of vehicle weight, the heavier vehicles produce more particulates in the same manner in which they produce more gaseous emissions. EPA certification-vehicle emissions data for the 1979 model year are presented in Table 3.

TABLE 3. LIGHT-DUTY VEHICLE PARTICULATE EMISSION RATES AS A FUNCTION OF VEHICLE TYPE AND WEIGHT*

Vehicle (Diesel)	Approximate Curb Weight, lbs	FTP Particulate Emissions Rate, gm/km
VW Rabbit	2000	0.14
Peugeot 504	3000	0.18
Mercedes 300 D	3500	0.52
Oldsmobile 4.3 l	3500	0.45-0.63
Oldsmobile 5.7 l	3800	0.53

Particulate emissions also appear to increase with increasing aromaticity of the fuel, with lower speed and load operations, with higher intake air temperature, with higher fuel temperature, and with the use of EGR (exhaust gas recirculation). The relationship between particulate emissions and EGR is an especially troublesome problem for the industry because EGR is currently the best hope for meeting the more stringent NO_x emission standard scheduled for the 1981 model year. EPA has proposed a particulate emission standard of 0.373 gm/km also to take effect in the 1981 model year; the industry claims that it cannot meet both NO_x and particulate standards in 1981 with current technology.

Data in the literature relating particulate emission rates to vehicle speed and load under steady state conditions is sparse. The following data may or may not be representative, but is presented in Table 4 to illustrate what is available.(3)

* Federal Register, Vol 44, No. 23, February 1. 1979

TABLE 4. LIGHT-DUTY VEHICLE PARTICULATE EMISSION RATES AND CONCENTRATIONS FOR CYCLIC AND STEADY SPEED OPERATION

	Particulate Emissions, gm/km (mg/m^3)			
Vehicle	1975 FTP	Low Speed	50 kph	85 kph
Mercedes 240 D	0.31 (97)	2.8 (83)	0.13 (70)	0.17 (95)
VW Rabbit	0.28 (100)	1.8 (46)	0.12 (78)	0.14 (87)

The values in Table 4 are averages of a number of tests, with individual test results sometimes varying quite widely. In general it appears that the low speed condition is the worst particulate emission mode in terms of gm/km although the particulate concentration is relatively low. Also, it is evident that steady speed/load conditions result in lower particulate emission rates than cyclic conditions.

SECTION 3

IN-STREAM OXIDATION OF PARTICULATE

One of the simplest control techniques would be an exhaust system that completes the combustion of the carbon particles. Some aspects of this method are explored below.

THERMAL IN-STREAM OXIDATION

One strategy for the control of diesel particulates is the use of in-stream oxidation. Since the exhaust always contains some oxygen, the diesel particulate can be eliminated by oxidation if the temperature is high enough and the time for burning long enough. However, raising the particle temperature by heating the bulk of the exhaust gas requires a large amount of energy. Since such very small particles will reach temperature equilibrium with the surrounding fluid very rapidly, the bulk of the gas must be kept at the temperature desired for the particles. Unless almost all of the energy used to heat the bulk gas could be recovered, this method of control would be quite impractical. Design of a compact heat exchanger for the temperatures and flow rates involved would be difficult.

The analysis below explores some aspects of in-stream oxidation of particulate. The following exhaust conditions are assumed:

exhaust temperature	200 C
exhaust flow rate	0.05 kg/s
particle size	1 μm, 0.1 μm or 0.0287 μm*
particle concentration	100 mg/m^3

* Particles of this size are estimated to have a surface area of 112 m^2/g. Lee, Thring and Beér[4] report that soot from a hydrocarbon flame has a BET surface area of 112 m^2/g. Surface areas for various diesel particulates need to be measured in order to refine these calculations.

These conditions might represent a 5.7 l diesel engine at medium speed and high load.

The particles must be kept at a high temperature long enough to allow oxidation to take place. In order to get an idea of how much time is available, exhaust velocity of 21 m/s was calculated based on a 50-mm ID exhaust pipe. If the path at the high temperature is 1-m long then the time available for oxidation will be 50 ms. This does not take into account the additional residence time in the muffler or in a control device, but it does illustrate magnitude of the time available.

The residence time at high temperature could be increased by increasing the volume of the afterburner device. However, since the possibility exists that the engine may supply a flammable mixture to the exhaust system, a large confined volume would present a safety hazard.

For particles in this size range the rate of oxidation should be kinetically controlled at all reasonable temperatures[5]. Thus, by examining the chemical kinetics, the temperature necessary for oxidation in this time interval can be determined. Good data for the oxidation of diesel particulate is not available, so this calculation was carried out using data for graphite. It was also assumed that the particulate consisted of small spheres. The kinetic expression of Nagle and Strickland-Constable[6] is used for these calculations. This expression gives the mass of carbon oxidized per unit surface area per unit time at a given temperature and partial pressure of oxygen. For this type of rate expression

$$\frac{dm}{dt} = RS \text{ or } dm = RS\, dt$$

where m = mass of carbon burned
t = time
R = reaction rate
S = surface area

Since for a sphere $S = \pi D^2$ where D = sphere diameter

$$dm = R \pi D^2 dt$$

To find the change in sphere volume we note that:

$$\frac{dV}{dD} = \frac{\pi D^2}{2}$$

By considering the change in surface area with diameter, the burning times of the particles can be found. The following expression results:

$$t = \frac{\rho D_o}{2R} \qquad (I)$$

where ρ = density of carbon
D = particle diameter
R = reaction rate

Using equation (I) and the kinetic expression of Nagle and Strickland-Constable the time required to oxidize completely a particle of a given size can be found. Some results of this calculation are shown below:

Particle Size	Temperature	Burning time, approx.
1 µm	1000 K (727 C)	20 s
1 µm	1500 K (1227 C)	1 s
1 µm	2000 K (1727 C)	50 ms
0.1 µm	1000 K (727 C)	2 s
0.1 µm	1500 K (1227 C)	100 ms
0.1 µm	2000 K (1727 C)	5 ms
0.0287 µm	1000 K (727 C)	575 ms
0.0287 µm	1500 (1227 C)	30 ms
0.0287 µm	2000 (1727 C)	1 ms

It can be seen from the above results that the particle temperature must be quite high to complete oxidation in a reasonable time. It is of interest to estimate that heat required to bring the exhaust to this temperature.

To heat a kg of exhaust from 200 C to 1200 C requires about 1120 kJ of heat. At an exhaust flow of 0.08 kg/s, 90 kJ/s of heat must be supplied.

At this speed and load the engine uses about 13 kg/hr of fuel or 0.0036 kg/s. If the heat content of the fuel is taken as 45,000 kJ/kg, then the engine is using 162 kJ/s of energy. It can be seen that the energy required to heat the exhaust to the particulate burning temperature is over half of that used by the engine. This is obviously unacceptable.

It might be argued that heat will be released when the particulate burns. The heat released will be given by

$$\dot{Q} = \dot{m}_p H$$

where $\dot{Q}$ = heat released

$\dot{m}_p$ = mass flow of particulate

$$= \left(\frac{100 \text{ mg}}{\text{m}^3 \text{ sec}}\right) \left(\frac{\text{m}^3\text{ex}}{0.737 \text{ kg ex}}\right) \left(\frac{0.08 \text{ kg ex}}{\text{s}}\right) = 11 \text{ mg/s}$$

H = heat of combustion for particulate

Assuming that H is 45,000 kJ/kg, we find 0.5 kJ/s released by the burning particulate. It can be seen that this is negligible compared with the 90 kJ/s required to heat the exhaust.

If it were possible to recover most of the heat in the hot exhaust, this afterburning concept might be feasible. Some kind of heat exchanger would be required for this purpose. This heat exchanger would have to operate at temperatures of 1200 C and durability may be a real problem.

CATALYTIC IN-STREAM OXIDATION

The burning rate of the diesel particulate appears to be not rapid enough at typical exhaust temperatures to eliminate a significant amount of particulate. One way to speed up a reaction rate would be to use a suitable catalyst.

Such a catalyst would, of course, have to be incorporated in the particle as it is formed. This suggests that the catalyst be an additive to the diesel fuel. Although the exact mechanism that would cause incorporation is not known, several could be suggested involving either chemical reaction of the soot with the additive, agglomeration of soot and additive particles, additive particles acting as nuclei for soot formation, or adsorbtion of the gaseous additive by the soot. If such incorporation can be achieved and a suitable catalyst found, the burning rate at exhaust temperatures could increase dramatically.

There are a number of metals that show catalytic activity for the oxidation of graphite. Some likely candidates are discussed in detail in connection with the oxidation of material collected on traps. As the following tabulation[7] shows, the reaction rate can increase dramatically. And we can expect that the presence of the catalyst will be most noticeable at lower temperatures.

Metal	Rate of Reaction Relative to Pure Graphite
Ba	100
Na	230
Au	240
V	340
Cu	500
Ag	1,340
Cs	64,000
Mn	86,000
Pb	470,000

There would be toxicity problems with some of these metals, but others may be acceptable. Even lead may be acceptable since the amount required may be very small--in tests with graphite a lead concentration of 1.3 ppm was enough to increase the rate of oxidation at 430 C by a factor of 120.

Exactly how large an increase in the rate of oxidation will occur is uncertain. One reason is that the impurities and trace elements in the diesel fuel may already be acting to catalyze the oxidation reaction. It has been suggested that this is the case for most coal combustion where the measured energy of activation is about 170 kJ/mol although the energy of activation of pure graphite is reported to be 250 kJ/mol. Certainly diesel fuel does not have as many metallic impurities as coal and probably lacks the optimum amount of metallic catalyst.

Such a catalytic approach could make in-stream oxidation of the diesel particulate feasible. This would have the advantage of not requiring any add-on devices. Or, if a trap were found necessary, the particulate loading would be reduced, and the light-off characteristics would be improved.

SECTION 4

OXIDATION OF FILTER-TRAPPED PARTICULATE

A basic problem with the particulate in the diesel exhaust is that it is too dilute to burn. This can be remedied by collecting the material on a filter. Although a filter is usually thought of as a way to remove particles from the flowstream, it can also be thought of as a device for concentrating the particulate material. In this concentrated form the average heat loss is reduced and conditions for combustion are more favorable. In fact they may be so favorable that damaging temperature excursions may occur.

TRAP/OXIDIZER STRATEGIES

There are a number of design concepts for trapping and oxidizing the particulate emissions from diesel engine operation. Although the requirements for successful application of each of these concepts can be described qualitatively, neither the character of the particulate, the service require-

ments, nor the limitations imposed by automobile application are well enough described to permit firm choice among these concepts of the complete rejection of any. Some concepts, such as the catalytic oxidation of a solid carbon particle that has been casually deposited on a solid catalytic surface, immediately imply such severe limitations as to appear improbable. In this section of the report it is assumed that the particulate has been trapped in a fashion suitable to each concept.

Four broadly based strategies must be considered:

Strategy 1 - The trapped particulate is brought to ignition by heat derived from the engine operation, usually from the hot exhaust gases themselves.

Strategy 2 - The trapped particulate is brought to ignition by an auxiliary heating device used to trigger ignition at programmed times in the engine operation cycle.

Strategy 3 - The particulate is brought to ignition at substantially lower temperatures than either of the above cases by use of catalytic materials that promote particulate oxidation.

Strategy 4 - The condensible portion of the material forming the ambient particulate is first oxidized (catalytically), then the remaining particulate is burned in a trap-oxidizer unit according to any of the above three strategies.

These four strategies are used as a vehicle to discuss the problems and critical features associated with the burning of trapped particulate emitted by automotive diesel engines. It is probable that any of these strategies might be applied successfully in the laboratory; the primary source of the difficulties that arise is the automobile application with its adjunct limits on space, cost, and energy consumption.

In any of these choices the trapped particulate must be ignited and burned, and the implications of this are basic to all strategies. In the next section a kinetic model for ignition is discussed.

The Ignition Concepts

The trap/oxidizer type of particulate control device is basically a chemical reactor in which oxidation occurs. The rate of oxidation will vary with the temperature--as the temperature increases, the rate increases rapidly due to the exponential nature of the kinetic rate expression. Eventually, the rate of the reaction is limited by mass transfer (diffusion of oxygen to the reacting surface and reaction products away from the surface), and no longer increases with temperature. As the temperature rises the heat loss from the device also rises. Thus, the operating temperature will be that temperature for which the heat released by the reaction is equal to the heat loss. Because the reaction rate curve flattens at high temperatures, the

heat loss curve intersects in two places and the device will tend to be in one of two conditions--unignited or ignited. Once ignition occurs the temperature very rapidly reaches a value near the combustion temperature of the fuel. This is because the exhaust flow through the filter bed serves to increase mass transfer to the carbon on the filter. Thus, the mass transfer limitation is not severe. Also, the heat loss occurs at the surface of the device and conditions at the center will be near adiabatic. So the two things that tend to limit the temperature are not very effective. The ignited condition therefore may destroy the control device.

Application of chemical reactor theory allows a more detailed picture to be drawn.

Salient features of any exothermic reaction (e.g., combustion or oxidation) in a flow-through reactor are the transient nature of both the temperature of any volume element with time, and the large gradients of temperature throughout the reactor. Afterburners, whether catalytic or not, exhibit ignition characteristics similar to flame processes and the performance of the afterburner is directly related to the achieving and stabilizing of a suitable "ignited" state.

The situation for some volume element of the reactor is described with the help of Figure 2 using theory similar to that employed by Wagner[7] and Frank-Kamenetskii[8]. The rate of heat generation ($\dot{Q}_I$) in some small volume element is described by Curve 1 which exhibits the anticipated exponential rise in reaction rate with temperature at the lower end and the levelling-out effect at the upper end due to transport limitations. An increase in reaction kinetics would be expected to move the lower end of the curve upward, as illustrated by Curve 4, and an increase in transport flow or an increase in combustible concentration would raise the upper end, as illustrated by Curve 3.

For the given volume element, temperature stability is achieved when the rate of heat generation, $\dot{Q}_I$, equals the rate of heat loss from that volume element, $\dot{Q}_{II}$, due to the sum of the processes of convection, conduction, and radiation. In Figure 2, Curves 5 and 6 represent situations created by different levels of the heat loss processes, $\dot{Q}_{II}$. The heat loss curves are much straighter than those for $\dot{Q}_I$ since conduction and convection tend to be more linearly related to the ΔT generated. Significant contributions by radiative processes at high temperatures would make the $\dot{Q}_{II}$ curves concave upward. In the example of Figure 2 the heat loss relationships are shown as straight lines.

Figure 2 can be used to demonstrate how the stable operating temperature of the exothermic reactor, here assumed to be catalytic, will vary with the initial temperature conditions. In each case the intersection of the assumed $\dot{Q}_I$ and $\dot{Q}_{II}$ curves represents the stable operating temperature for the volume element under consideration.

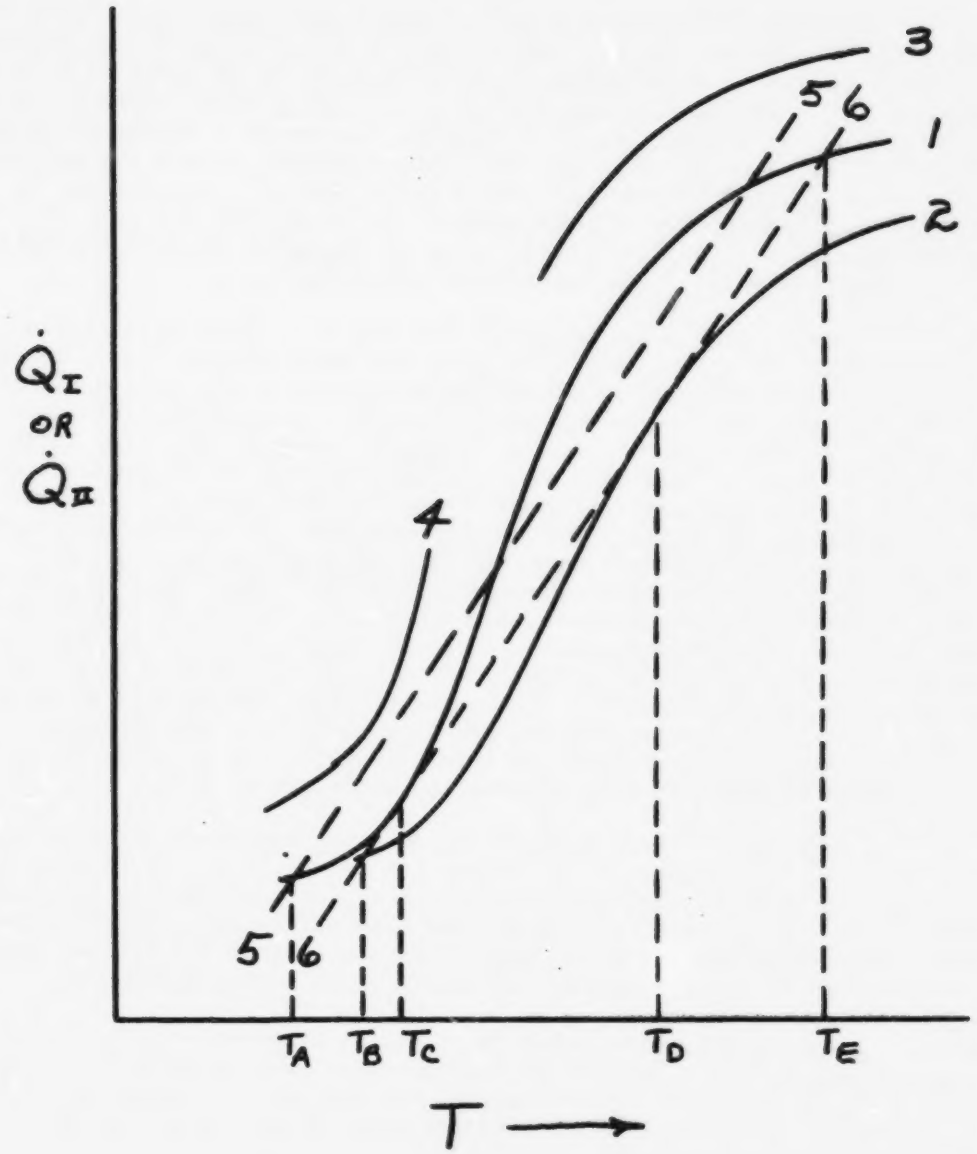

FIGURE 2. TEMPERATURE RELATIONSHIPS FOR EXOTHERMIC REACTORS

For a cold start with catalytic surface temperature less than T_A, and assuming Curves 1 and 5 are valid, an inlet gas with temperature less than T_A but no further, since above T_A the rate of heat loss exceeds the rate of heat generation.

Incremental decreases in the rate of heat loss would raise the operating temperature, T_A, by moving Curve 5 toward Curve 6. An equivalent effect on operating temperature would be achieved by an increase in heat release, e.g., by raising Curve 1. When the circumstance represented by T_C is reached as a result of such changes, the system temperature is no longer stable since any further temperature increase causes the operating temperature to rise continuously until T_E is reached. Temperature T_C is the ignition temperature for the system. It is usually the case that T_A is not enough to give a "practical" rate of oxidation so that the ignited state, represented by T_E is the one that is sought.

Later, decreased catalytic activity or a lower combustible concentration can cause Curve 1 to bend over more sharply (e.g., to Curve 2) until a tangential situation analogous to that of Curves 2 and 6 is generated. The new temperature represented by the tangential contact of $\dot{Q}_I$ and $\dot{Q}_{II}$, T_D in Figure 1, is the "flameout" temperature. Any further decrease in reactor temperature causes the steady state temperature to fall abruptly to the lower intersection at T_B, and again all intermediate temperatures are unstable. This is the ignition characteristic commonly observed for exothermic reactors, whether catalytic or not, and the stable upper operating temperature, the "ignited" condition, in many cases tends to approach the adiabatic temperature that can be calculated for the fuel/air mixture represented. This is especially true for local catalytic sites where the heat of reaction is momentarily shared by a relatively few atoms of the adsorbed gas and the catalytic site. Thus, frequently it is a good assumption that if the catalytic reactor, here the afterburner, cannot tolerate the adiabatic combustion temperature for the fuel/air mixture represented it probably will deteriorate seriously in activity during use.

For oxidation processes such as this, catalysts serve to lower the ignition temperature of the combustion system, e.g., by raising Curve 1 in Figure 2, but the thermal (noncatalytic) processes tend to predominate kinetically at T_E. For this reason the catalyst is best viewed in most of such cases as an igniter which must be stable against the thermal combustion temperatures of the system represented if it is to be reused.

In applying this model for ignition processes to the diesel particulate oxidation problem we must consider several cases and keep in mind that the catalyst employed may or may not be a preformed solid body contained in the afterburner. Consideration of these several cases helps to outline the possibilities available.

Strategy 1 - Thermal Ignition of Trapped Particulate

Experimental trials in the BCL Laboratory indicate that accumulations of diesel particulate ignite at temperature of about 600 C. Below this temperature oxidation rates appear very slow and the results seem to confirm the expectation that only the ignited condition will serve this purpose. Such temperatures are unrealistically high for any reliable mechanism whereby the particulate is regularly ignited by waste heat from the engine without some assistance. No further consideration is given to this strategy but the temperature cycle for the exhaust gases can serve as the basis for more frequent and/or scheduled ignition in the options discussed for the other strategies.

Strategy 2 - Use Ignition Devices

Since the heat from the engine alone is insufficient to ignite the deposit of particulate material on the trap, some type of ignition device must be used. One possible device is a glow plug-type of electric resistance heater. The basic problem with this strategy is that the automotive electrical system is not capable of delivering an amount of energy that is significant compared with the energy that might be lost to the relatively cool exhaust flowing through the device. For example, the electrical system is hardly able to supply more than 1 kW or 1 kJ/s. Something like 50 kJ/s would be required to heat the exhaust stream to the deposit ignition temperature. Obviously this is not the purpose of the ignition device. The point is that if one tried to heat the entire deposit on the trap to the ignition temperature, the heat losses to the exhaust would be too large. The only alternative is to provide a few hot spots in the deposit and let the combustion propagate through the remainder. This could present a problem, since the deposit must be sufficiently evenly distributed for this propagation to occur. If it is not, fuel may accumulate in part of the trap, only to ignite in an unscheduled or uncontrolled fashion.

Alternatively some diesel fuel could be burned to raise the trap/oxidizer device to its ignition temperature. The diesel fuel would, in turn, be ignited by a spark. This approach has a number of advantages. The amount of heat that can be put into the system is large. The fuel is already at hand. A spark ignition system should pose no problems. Since the additional fuel needs to be supplied for only a few seconds, the effect on overall fuel economy will be small.

There will be design problems, however. The fuel spray must ignite smoothly--a controlled addition of heat is required, not a backfire. The fuel would probably be added with a small spray nozzle; this nozzle must not foul when not in use. The heat from the burning ignition spray must not harm the device--the additional heat may make burn-off temperatures even higher. The presence of another fuel and ignition system adds cost and complexity.

Either system would need some kind of control to insure that ignition occurred at necessary intervals. This could be done on the basis of engine hours, pressure drop across the device, miles traveled, or fuel used. Because of the wide variation in ambient conditions, it is anticipated that the control system will have to be set for worst case conditions with extra cycles at other times.

It seems then, that there is no barrier to making an auxiliary ignition device for the trap/oxidizer. Of course it would be more desirable that the device stand alone. If the ignition temperatures were lower, additional ignition would not be necessary. It is possible that a catalytic approach may help here.

Strategy 3 - Catalytic Ignition of Particulate

For the present application, the catalytic effect must be obtained at the surface of carbon particulate at temperatures less than that at which the unassisted thermal oxidation is detectable. The heat release rate due to this catalytic oxidation must be sufficient to achieve the ignition temperature described earlier. Trials[10] of the uncatalyzed ignition of furnace soot placed the ignition temperature (point C in Figure 1) at 615 C, and it was observed that insignificant oxidation rates were obtained below 480 C. This helps to define the position of the Q_I curve in Figure 1. The reduction of inlet oxygen concentration from normal air to 8 percent had little effect on the ignition temperature for untreated samples. Samples treated with certain inorganic salts showed substantially lowered ignition temperature, but the reduced O_2 content caused these ignition temperatures to rise somewhat above those found in normal air. These catalysts are discussed in the following paragraphs.

Both the design of the catalytic chamber and the activity of the catalyst influence the ability of the chamber to achieve this ignition. Once the most favorable form of catalysis is identified a study of chamber design must be undertaken to maximize the repeatability of the catalytic ignition at acceptable performance levels.

The oxidation of a solid carbon particle casually implanted on a solid catalytic surface is most difficult to catalyze since the contact between the particle and the catalyst is uncontrolled and its area is anticipated to be small. The presence of hydrocarbon condensate in that carbon particle (as in diesel particulate) may alleviate this difficulty somewhat since that condensate may transfer to the catalytic surface and the higher H/C ratio, expected for the condensate as compared to the solid carbon portion, augments both the rate and heat release of the catalytic oxidation. This anticipated influence of the level of condensate accumulation on either the thermal or catalytic ignition of diesel particulate does not appear to have been examined systematically.

In some unspecified temperature range the condensate may be anticipated to accumulate rapidly on the particulate as the temperature falls, but this same fall in temperature increases the level of catalysis that will be needed for ignition. In the diesel exhaust situation the temperatures that can be relied on are already lower than desired for reliable ignition and so catalytic trap-oxidizers have not been easy to develop. Catalytic oxidizers for hydrocarbon vapors located as close to the exhaust manifold as possible have been reported effective for oxidation of the condensate portion of the particulate without materially oxidizing the solid particulate itself[11]. Such experience implies that the condensation of hydrocarbons onto the particulate was not yet complete at this stage of the exhaust system. Catalytic oxidizers of this sort function by adsorption and oxidation of hydrocarbon vapors and are not necessarily designed as particulate traps. These units in themselves are not sufficient for the particulate problem under consideration but will be considered further in Strategy 4.

The only form of catalysis that has been described in any detail for oxidation of carbon particulate is that developed years ago for removal of soot accumulation from flues and furnaces by the use of inorganic salts. The U. S. Bureau of Mines Bulletin 360[10] and the more recent work of Duval[7] and coworkers provide an understanding of the level of development of this form of carbon particulate oxidation catalysis.

It is of interest to note that English patents for inorganic soot removers began to appear in 1856 covering the use of ordinary alkalis or salts such as NaCl, quicklime plus soda ash, magnesia, copper salts, and others. American patents started in 1892 covering similar compounds and especially chlorides of a number of elements such as zinc. From the earliest patents the use of chlorides has been favored for such purposes. Bulletin 360 of the U. S. Bureau of Mines lists 59 compositions tried by them and exhibiting decreases in ignition temperatures of as much as 287 C. By this means the ignition temperature was lowered from 613 C to a minimum of 326 C in normal air. Simple salts such as ammonium chloride and CaCl lowered the ignition temperature 137 C and 92 C, respectively.

In all of these tests the volatility of the salt used was an important characteristic. Initially, the salt was applied by vaporizing it and allowing it to deposit onto soot that had been accumulated previously on a test screen. The action by which the salt catalyzed burning was not specified, but some relatively contemporary publications suggest mechanisms that do not seem to have been further investigated.

Thus, Cassel[12] noted that soot deposited on the etched or ground surfaces of Jena glass ignited much more easily and burned more rapidly than soot on adjacent smooth surfaces of the glass. From evidence for oriented crystal growth of soot particles on surfaces he suggested that the ground surfaces interrupted crystal growth during soot deposition because of surface irregularity, and also helped to prevent secondary crystal growth during oxidation (burning). He reasoned that the salt deposits condensed on soot similarly promote ignition and burning by maintaining the highly dispersed soot structure prior to and after ignition.

Alternatively, Taylor and Neville[13] and later Day, et al.,[14] noted large increases in soot burning rate following deposition of soot onto surfaces previously coated with salts by evaporation. Both of these investigations concluded that the salts probably functioned by hastening the decomposition of carbon-oxygen surface complexes. With this barrier removed the carbon surface was believed to be more readily attacked by oxidizing gases. A brief review of the succeeding years publications has failed to disclose any further discussion of these or other hypotheses for the action of the salts. It is of interest to note that the promotion effect is claimed either for salts vaporized onto the soot or for soot condensed (deposited) onto the previously deposited salt. In the more recent work of Duval and coworkers[7] inorganic cations were impregnated into graphite carbon from water solution and then the rates of oxidation were noted. The results showed that the introduction of cations at 120 ppm concentration produced rates of oxidation up to 470,000 times that of the untreated graphite. In this study the effective cations were identified as representing those elements that have variable oxidation states, and can exist in defect states of oxidation. By this means they serve as oxygen carries to the graphite interface.

Table 5 shows an interesting contrast in the relative effectiveness of the various metal salts employed in the studies of impregnated graphite and of vapor deposited compounds on soot particulate. The differences seem to underline differences in mechanism of action that have occurred, either because of the difference in method of application or more probably because of the differences in reactivity and structural stability of soot and graphite. The variable valence postulate for the catalytic action on graphite is the same as that widely used to explain the catalytic action of high-surface-area oxide catalysts in catalytic hydrocarbon oxidizers. Two additional observations are of interest here:

1. Some of the most active catalytic materials for solid catalysts in catalytic oxidizers, i.e., the platinum metals and cobalt oxides, were not tried.

2. Low melting oxides, such as lead oxide, have low activity in solid-state catalytic oxidizers in spite of their usefulness as oxygen carriers because on melting they destroy the high area dispersion needed for the solid-vapor contact between catalyst and reactant. In the present application the support for the catalyst is the reactant (carbon) itself and the ease of melting may imply good dispersion and mobility for the catalyst on the oxidizing graphitic interface.

The large increases in oxidation rate illustrated by these catalytic applications indicate that considerable catalytic assistance is available for the burning of diesel-exhaust particulate.

TABLE 5. RELATIVE ACTIVITY ESTIMATES FOR CATALYTIC INORGANIC COMPOUNDS ADDED TO CARBON

	Lowering of Ignition Temperature °C(1)	Relative Oxidation Rate(2)
Na	92	230
Ca	124	4
Zn	130	--
Mn	130	86,000(3)
Fe	131	--
K	137	--
NH_4	137	--
Sn+2	153	--
Ni	162	32
Pb	180	470,000(3)
Cu	284	500
Ba	--	100
Au	--	240
V	--	340
Ag	--	1,340(3)
Cs	--	64,000(3)

(1) Compound added to soot particulate by vaporization of the corresponding chloride.(9)

(2) Compound added to graphite powder by impregnation of a soluble salt. Oxidation rate compared to untreated graphite.(6)

(3) For most of these elements the normal oxide structure melts below 500 C; in the case of Mn a series of defect oxides are known with uncertain melting points. All of these elements exhibit thermal decomposition of normal oxide structure at or below 500 C.

Preformed catalyst surfaces, even if effective, may be anticipated to accumulate ash residues from lubricating oil and/or fuel components of the particulate and the active life of such surfaces may be materially shortened by such accumulations. On the other hand, catalysts incorporated in the particulate by inorganic residues from fuel or oil additives, by spray application or by vaporization onto the accumulating particulate are self-renewing and should occupy very little residual volume once burning is complete. The effectiveness of such inorganic catalyst applications for burning of diesel exhaust particulate should be easy to demonstrate. The means for application of such catalytic methods to automobile service remains to be examined.

Strategy 4 - Combined Use of Catalytic Hydrocarbon Oxidizer and Particulate Trap/Oxidizer

The condensate portion of diesel particulate is a potential problem in operation of the trap/oxidizer because of its volatility. Balanced against the usefulness of the condensate for promotion of ignition is the possibility that partially oxidized portions of this condensate may be re-evaporated from the advancing combustion front and emitted with the exhaust gases. Some recent reports indicate that such re-emitted material may be highly toxic. Elemental carbon can be expected to burn largely to CO, CO_2, and H_2O and we anticipate that the troublesome re-emissions derive from the condensate portion of the trapped particulate.

Separate oxidation of the condensibles would reduce the mass load on the trap oxidizer by 5 to 40 percent depending on the engine operation conditions. The question arises then of the degree to which separate oxidation is feasible and the effect of that oxidation on the particulate trap. The published experience[11] with catalytic hydrocarbon oxidizers for stationary diesel service seems to imply that the condensation of hydrocarbons onto the particulate has been far from complete when the oxidizer is located as close to the exhaust manifold as possible. These units, built for minimum back pressure, do not function as particulate traps so that the hydrocarbon portion apparently is being oxidized at a catalyst surface without any effective retention of the solid particulate. Thus, Sercombe[11] has described a platinum catalyst system that is claimed to provide overall control of hydrocarbon, nitrogen oxide, and CO emissions from diesel engines but which apparently has no effect on the particulate. Similarly, another hydrocarbon oxidizer system was described[15] as able to remove 70 percent of the hydrocarbon emissions from diesel engine that, without the oxidizer, produced particulate with 35 percent condensibles. Catalytic hydrocarbon oxidizers of this sort perform well only if "ignition" is attained and maintained, and failure to achieve this may have contributed to the comparatively poor performance of the oxidizer tried by Seizinger, et. al.,[16] in their trials of two derated diesel engines operating at low emission levels.

Condensation Effects on Particulate

As the temperature falls the least volatile portions of the condensibles may be anticipated to collect first in liquid form in the micropores of the soot particulate. Micropores in the particulate might be expected to cause condensation of a vapor, whose liquid form is capable of wetting the surface of the particulate, at partial pressures only a few percent of the saturation vapor pressure of that vapor. As the exhaust gases cool, this condition would be reached first for the least volatile components and would cause condensation of that vapor at temperatures well above the dewpoint of that vapor.

On the other hand, as condensation proceeds with falling temperature, each particle of solid carbonaceous material can serve as a condensation nucleus for the condensable vapor, even though the pores of the particle may be already filled with condensate. Because of the small size of the elementary particles of diesel particulate, e.g., 200 Å, this condensation would be occurring on convex surfaces of small radii and would proceed only at temperatures somewhat below the vapor dewpoint. Here the concept of critical size for condensation nuclei applies: vapor pressures on convex surfaces of small radii are greater than those over surfaces of larger radii so that condensation will start on the biggest particles and, for some given condition, may proceed only on particles larger than some critical size. Thus, if there is time for these fractional condensation processes to occur, we can anticipate differences in amount and in composition of condensate in particulate fractions of different size and structure. The steepness of the temperature gradient for the exhaust stream would be the determining factor here.

Assuming that the exhaust condition can be obtained where condensibles have not yet been incorporated into the particulate, a catalytic hydrocarbon oxidizer can be expected to be able to oxidize this organic portion of the exhaust without being effective as a particulate trap. The longevity of such units may be a problem if the ash content of the exhaust accumulates on that catalyst as part of the organic phase being oxidized. On the other hand, if the ash is not collected but remains part of the particulate that passes through, the poisoning action of the ash may not be serious. These features must be investigated. The remaining particulate with condensibles largely removed could be trapped and oxidized, probably by Strategies 2 and/or 3. The relative difficulty of ignition of such particulate remains to be demonstrated; in any event a combination of Strategies 2 and 3 seems best for the particulate trap-oxidizer.

APPROACHES TO TRAP/OXIDIZER DESIGN

The trap/oxidizer is a chemical reactor in which oxidation occurs. As outline above such a reactor tends to be in either an ignited condition or an unignited condition. When the device is in the ignited condition, the temperature very rapidly reaches the combustion temperature. The ignited condition therefore may destroy the control device.

Application of chemical reactor theory, along with data on the heat transfer, mass transfer and chemical kinetics of the device would allow a quantitative analysis of the above phenomena.

But even in the absence of such an analysis, it is clear from the experience that is available for trap/oxidizers that the qualitative picture presented above is correct and that ignition of the particulate often destroys the device.

In view of the above, a number of approaches to trap/oxidizer design present themselves.

- If the flow through the device were stopped when ignition occurred, the mass transfer limitation would occur at a lower temperature. This could be accomplished by temporarily bypassing the device, or by switching to an alternate. A possible disadvantage of this approach is that the combustion reaction will be oxygen-starved and may produce noxious products.

- The heat transfer can be increased. The critical area is in the center of the reactor where conditions are adiabatic rather than at the edge. The solution is to make the reactor all "edge", that is, to increase the surface to volume ratio. This could be done by making a flat pancake-shaped device or by including cooling passages in the internal structure. It would be desirable that each filter fiber would be able to "see" a relatively cool wall, and thus be cooled by radiation.

- The chemical kinetics could be changed through use of an inhibitor. The rate of reaction at a given temperature would be less and there would be more time for the heat to dissipate, thus making the device temperature lower.

- The situation can be accepted as unchangeable and the filter designed to withstand the temperatures expected during burn-off. It may well be that ceramic fibers would have the necessary ability to keep their integrity when very hot.

- The device will proceed to the adiabatic flame temperature only if a sufficient supply of fuel is available. If by the time the temperature had reached T_D on Figure 2 all the carbon had been oxidized, the high temperature of point T_E would never be reached. Also the reactor does not consist entirely of fuel, but contains the filter as well. The filter has a small thermal mass that requires heat energy to be raised in temperature. Thus, this approach would be to insure that the trap/

oxidizer always runs out of fuel before reaching a temperature that would be too high for the filter. The oxidation would never reach steady-state. This might be accomplished in a number of ways.

- If ignition occurs frequently enough, the amount of fuel accumulated will necessarily be small.
- Frequent ignition would be encouraged by the presence of a catalyst.
- Fuel could be added to the exhaust and ignition supplied regularly.
- The thermal mass can be deliberately increased. Ceramic "marbles" might be "mixed" with the filter to insure that the fuel was gone before the ceramic (and the filter) were overheated.

A successful device might well use several of these approaches. However, each should receive a detailed evaluation to determine their effectivness.

COMBUSTION OF COLLECTED MATERIAL

A general discussion about the combustion of collected material must be prefaced with the warning that the physical configuration of the device will be a major factor in its operation. If particulate material is removed (say, by rapping) from a filter, it will be in some kind of container, and it will be in a thick layer (many particles thick). Thus, when this material burns the situation will be similar to the combustion of a piece of solid fuel. Just as a thin piece of wood will not support a flame if the heat loss is too great, a layer of particulate will not burn if too much heat is lost to the container. It is expected that it will be diffcult to strike a balance between maintaining combustion and preventing excessive temperatures.

SECTION 5

CONCLUSION

This report lists a number of conceptually different ways to attack the diesel particulate problem. Each of these concepts could become the basis for different ingenious applications of creative design. The acquisition of engineering data relevant to the various concepts will make that design effort easier and will suggest the concepts that have the greatest potential for success. The specific design will insure that success; it is difficult to consider this factor in a general evaluation.

With this caveat in mind, it appears that the catalytic oxidation of the particulate on some type of filter-trap holds the greatese promise for the removal and destruction of the diesel particulate. The key to the successful operation of such a device would appear to be frequent, if not continuous, ignition combined with filter fibers that maintain their integrity at high temperatures.

The work in progress, at Battelle and elsewhere, will help fill the need for a store of experience with these devices. This experience is needed both to identify the concepts worthy of future development and to identify the specific materials and dimensions of the final choice.

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